Design and Construction of a Simulated Evaporative Heat Exchanger for Testing the Mitigation Effects of Pipe Coatings on Mineral Scale Deposition

A Senior Project

presented to

the Faculty of the Materials Engineering Department

California Polytechnic State University, San Luis Obispo

In Partial Fulfillment

of the Requirements for the Degree

Bachelor of Science in Materials Engineering

by

Taylor J. Anderson

June, 2013

Approval Page

Project Title: Design and Construction of a Simulated Evaporative Heat Exchanger for Testing the Mitigation Effects of Pipe Coatings on Mineral Scale Deposition

Author: Taylor J. Anderson

Date Submitted: June 7, 2013

CAL POLY STATE UNIVERSITY
Materials Engineering Department

Since this project is a result of a class assignment, it has been graded and accepted as fulfillment of the course requirements. Acceptance does not imply technical accuracy or reliability. Any use of the information in this report, including numerical data, is done at the risk of the user. These risks may include catastrophic failure of the device or infringement of patent or copyright laws. The students, faculty, and staff of Cal Poly State University, San Luis Obispo cannot be held liable for any misuse of the project.

Prof. Blair London
Faculty Advisor

____
Signature

Prof. Richard Savage
Department Chair

____
Signature

Acknowledgements

This project was supported graciously by Drill Cool Systems, Inc. DCS was great to work with, especially Chris Balsillie who has been an ideal industry contact. I could not have asked for a better experience with a sponsor company. Rich Albert and Rick Maynard from DuPont were also generous in donating time and materials to make this project happen. Finally, a big thank you to Prof. Blair London for the enormous amount of time and care he devoted to me and my project.

Table of Contents

List of Figures

Abstract

The thermal efficiency of evaporative heat exchangers is diminishing due to mineral scale buildup on heat exchanger surfaces. A simulated evaporative heat exchanger was designed and constructed for testing the mitigation effects of polymer coatings on mineral scale deposition rates. The heat exchanger was designed to cool hot mud at 200°F using a cooling water supply with a calcium concentration of 1000 ppm. The system was constructed using 1.5-inch diameter polypropylene piping, a DIG Corporation drip irrigation system, a TotalPond 530 GPH pond pump, an Omega CSI32K miniature benchtop controller, Omega FWH321-020 high temperature heater tape, and fifteen copper pipe samples. DuPont™ lab technicians coated ten copper pipe samples with two different fluorinated ethylene propylene (FEP) polymer coatings: 954G-300 Teflon® FEP and 532-1003 Teflon® FEP. Both coatings were applied to the exterior of five copper pipe samples each (standard 1.25-inch diameter by 1-foot-long). Additionally, five separate foot-long lengths of 1.25-inch diameter copper pipe were used as is. A water solution containing 1 gram of calcium chloride ($CaCl_2$) per 1 liter of water was prepared to achieve a cooling water supply containing 1000 ppm calcium. This water solution was used in conjunction with the drip irrigation system and the pond pump to spray the exteriors of the coated and uncoated copper pipes. The heater tape was used in conjunction with the miniature benchtop controller in an attempt to maintain a pipe temperature of 200°F to replicate hot mud. The simulated evaporative heat exchanger was successful in uniformly delivering highly mineralized water onto heat exchanger pipes; however, the heater tape was unable to provide enough heat energy to maintain the desired temperature of 200°F.

Key Words

Materials Engineering, Hard Water Scale, Calcium Carbonate, Evaporative Heat Exchanger, Fluorinated Ethylene Propylene, Anti-scaling, Polymer Pipe Coatings

1 Introduction

1.1 Problem Statement

Drill Cool Systems (DCS, Bakersfield, CA) provides Geo-Coolers to clients around the world for mud cooling purposes. In these large evaporative coolers, water, from varying origins, cycles over long lengths of copper pipe. The water that is supplied often contains high mineral concentrations to the point that scale, primarily calcium carbonate, is deposited on the surface of copper cooling tubes by means of nucleation and growth. The initiating step, called nucleation, involves the adsorption of cationic (e.g., calcium) and anionic (e.g., carbonate) pairs onto the surface of the copper tubing, usually at surface imperfections. Crystal scale growth occurs as ion pairs continue to adsorb onto stabilized nuclei (nuclei that have exceeded a critical nucleus size). The thermal efficiency of copper tubing, which is essential to heat transfer, decreases with an increase in scale buildup; consequently, an unacceptable loss in the cooling efficiency of the system is experienced. Currently, scale buildup is removed directly by mechanical means, which is inefficient and costly due to the labor involved. The objective of this project was to develop a cost effective and robust solution to prevent hard water scale from forming on the copper piping or to make the scale deposit easily removable.

1.2 Drill Cool Systems, Inc.

DCS “offers drilling engineers the most advanced technology for safely and cost-efficiently completing geothermal, hot oil and gas well drilling operations.”[1] They provide two technologies, the Geo-Cooler drilling fluid chiller and the Insulated Drill Pipe (IDP) for use with on- and off-shore drilling and cooling. The IDP provides a technology that allows for the management of drilling fluid temperatures and protection of expensive electronics, drilling motors, and other vulnerable components in the drilling assembly that are sensitive to heat.[2] Essential to the IDP and its improved functionality is the cooling mud that is continuously pumped through the drill system and the associated Geo-Cooler that ensures the recirculating mud is properly cooled. There are a number of modes of failure for Geo-Cooler heat exchangers, namely a large efficiency loss is seen in heat exchangers that are exposed to highly mineralized water. In accordance with Det Norske Veritas (DNV) Certification, DCS products can be shipped anywhere in the world and are therefore exposed to a variety of environmental conditions. This can cause problems for the Geo-Coolers as they are often exposed to fresh water sources containing a variety of mineral ions at elevated concentrations. In other words, the Geo-Coolers are exposed to conditions in which a variety of mineral precipitates can form on heat exchanger surfaces, reducing the cooling efficiency.

1.3 Evaporative Heat Exchangers

An evaporative cooler is a heat exchanger that cools a fluid through the evaporation of water. These coolers take advantage of water's large enthalpy of vaporization, that is, water is able to absorb a relatively large amount of energy before transitioning from a liquid to a vapor. This results in a large drop in the temperature of the fluid being cooled.

The basic concept, design, and components of an evaporative cooler (Figure 1) are relatively simple. Additionally, as compared to other cooling methods (e.g., refrigeration) evaporative cooling is more efficient. It is estimated that the operating costs are one quarter that of a refrigerator.[3]

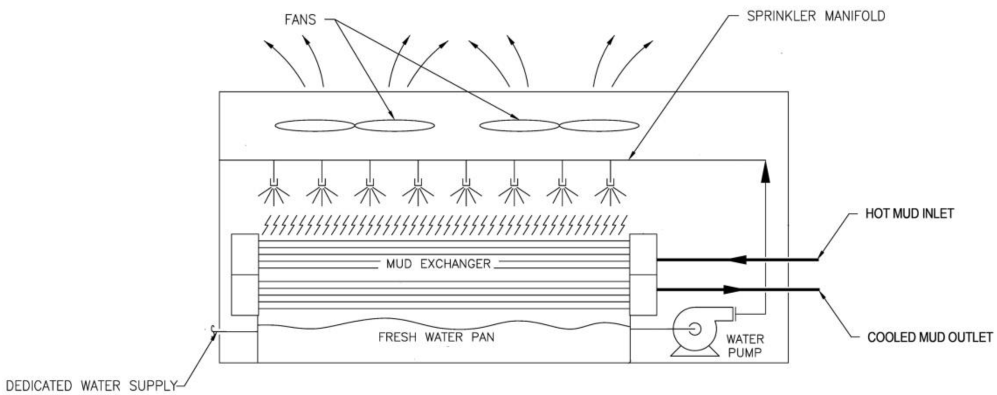

Figure 1: A schematic of a typical evaporative cooler. Hot mud is input into the system and flows through a bundle of copper pipes (mud exchanger), to be cooled. Cooling occurs when water is delivered, by the sprinkler manifold, onto the exterior surfaces of the copper piping in the mud exchanger. Heat is transferred from the mud exchanger surface to the water droplets in contact with the exchanger's surface. As water absorbs enough energy, it evaporates from the pipe's surface, thereby cooling the pipe and in turn, the mud.

DCS uses copper pipe as a means of transferring heat from the mud to the water because it has the second highest thermal conductivity of all metals.[4] Unfortunately, copper is susceptible to mineral scale buildup, effectively decreasing its thermal conductivity.

1.4 Hard Water Scale

Scale is the accumulation of natural minerals that precipitate out of solution and deposit onto a substrate. Commonly known as precipitation fouling, this unwanted solid accumulation is often seen depositing itself onto heat exchanger surfaces (including copper piping) reducing thermal efficiency, inducing corrosion, and costing the industry millions of dollars in lost production per year.[5]

1.4.1 Calcium Carbonate

While there are many minerals that form scale, calcium carbonate is the most prevalent and problematic. It is created when calcium ions in hard water react with carbonate ions, forming solid precipitates that deposit onto suitable substrates, for example, copper (Figure 2). This project focuses on and uses calcium carbonate as a model because it is the most prevalent and one of the most adherent scales, that is, it is a worst case scenario.[5]

Figure 2: Calcium carbonate mineral deposit on a DCS Geo-Cooler.

How do calcium and carbonate get into a water supply? Dissolved ions accumulate when groundwater comes in contact with certain rocks and minerals. One of these rocks, limestone, is composed largely of the minerals calcite and aragonite, both of which are crystal forms of calcium carbonate. When groundwater flows over limestone, calcite and aragonite dissolve into solution forming hard water. Furthermore, carbonate forms, through a series of reactions, from dissolved carbon dioxide that occurs naturally in all waters exposed to the atmosphere. The entire process (Figure 3) is constantly trying to find stoichiometric equilibrium by calcium carbonate either dissolving into solution or precipitating out of solution.

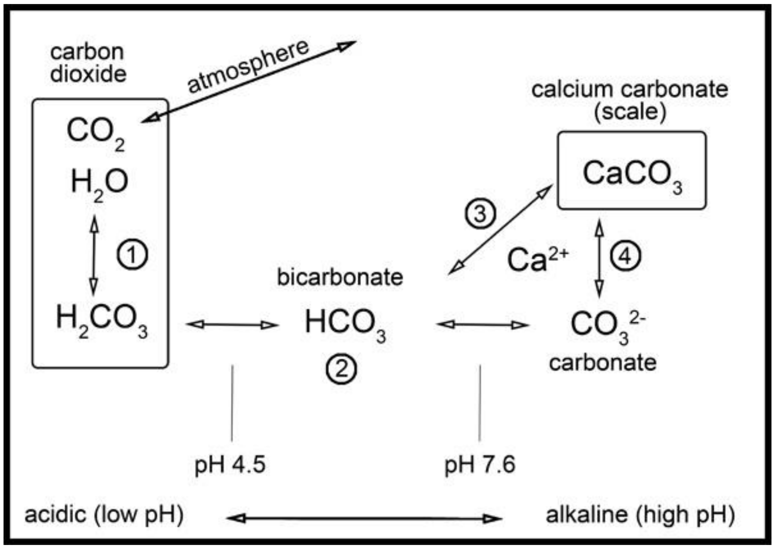

Figure 3: CO_2 from the atmosphere dissolves in water to form the acid H_2CO_3 (1). H_2CO_3 then dissociates further to produce HCO_3^- (2). HCO_3^- can breakdown into carbonate, which reacts directly with calcium to form calcium carbonate (4) or HCO_3^- can react directly with calcium to form $Ca(HCO_3)_2$, which in turn is broken down into calcium carbonate (3). These reactions are reversible and the direction they proceed depends on environmental factors, including pH and temperature.[6]

1.4.2 Scale Formation

The deposition of scale onto a substrate occurs when a solute capable of forming a deposit exceeds its solubility limit and becomes supersaturated. There are a number of conditions that lead to supersaturation; two, in particular, apply to evaporative heat exchangers. Heating a solution containing inverse solubility salts to a temperature above its solubility temperature and evaporating a solution beyond the solubility limits of the dissolved ions will both lead to mineral deposition.

Calcium carbonate scale has an inverse solubility effect, that is, solubility decreases as temperature increases.[7] This is particularly pertinent in heat exchangers where elevated operating temperatures are involved. The ions in solution with the cooling water become supersaturated as heat is transferred from the hot mud to the cool water. This causes precipitates to form on the surface of copper cooling tubes.

Sufficiently heating a solution will cause evaporation. In this case, heating a solution of water and calcium ions will cause the water to evaporate, effectively lowering the solubility limit of the calcium ions. In other words, if the solubility limit of a substance in one liter of water is reached and then half of the water evaporates, the substance would become supersaturated, thereby forming a precipitate. The deposition phase of this process can be explained step-wise. As a hard water droplet evaporates off of a heat exchanger surface, the solubility limit of calcium is reached. This calcium rich, supersaturated water droplet will react with carbonate, forming precipitates until either reactant is depleted. At this point, there will be a smaller water droplet (much of the water has already evaporated) filled with suspended calcium carbonate precipitates. The water will continue to evaporate until the precipitate is left behind. Now, the precipitate will either react with and adhere to the copper substrate or it will fall off.

The precipitation and deposition process occurs by means of nucleation and growth. The initial step, called nucleation, whose driving force is supersaturation, involves the adsorption of cationic (e.g. calcium) and anionic (e.g. carbonate) pairs onto the surface of the copper tubing and occurs either homogeneously or heterogeneously (Figure 4).

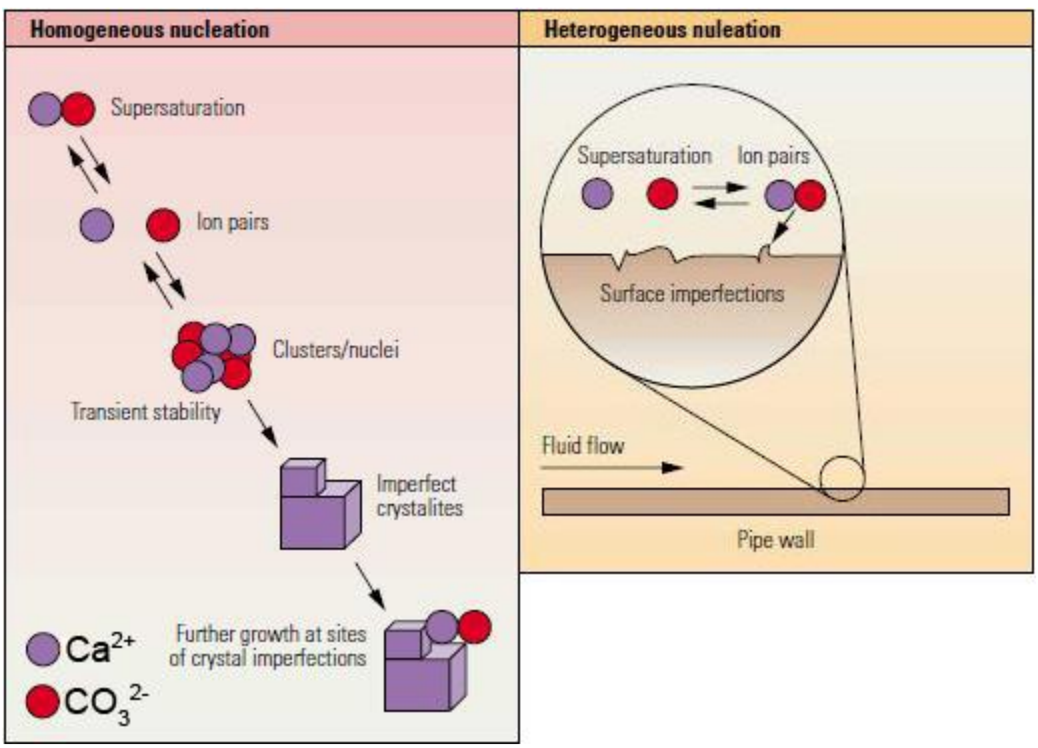

Figure 4: Depiction of homogeneous and heterogeneous nucleation in scale formation.[5]

In homogeneous nucleation, a supersaturated fluid will form unstable clusters of atoms that gain transient stability through localized fluctuations in equilibrium ion concentrations. These seed crystals grow by ions adsorbing onto imperfections on the crystal surface. Reduction in surface free energy is the driving force for crystal growth; as the crystal grows the surface energy decreases, increasing stability. Once the critical radius size is reached, the crystal becomes stable and will not dissolve back into solution. Alternatively, heterogeneous nucleation may occur. This includes crystal growth, similar to that in homogeneous nucleation, at surface imperfection sites on the substrate. In both cases, surface geometry and surface energy are the factors affecting deposition. Consequently, finding a scale mitigation solution lies in modifying the surface geometry and reducing the surface energy.

2 Experimental Procedure

2.1 Polymer Coatings

To limit surface roughness, imperfections, and energy, polymer coatings were considered as a solution. Specifically, the main consideration made was how to significantly lower the surface energy of the heat exchanger surface without increasing surface roughness or introducing significant surface imperfections. The appeal of using polymers is their ability to be versatile and cost effective.

2.1.1 Fluorinated Ethylene Propylene (FEP)

A number of fluoropolymers were considered because of their low surface energies. According to Rick Maynard, a DuPont Performance Coatings employee, FEP coatings show good adhesion properties to copper through its cure (500°F) while satisfactorily maintaining the desired low surface energy properties (surface energy of 18-22 mJ/m^2).[8] The C-F bond (figure 5) is the strongest single bond in organic chemistry and is the reason FEP is so nonreactive.[9]

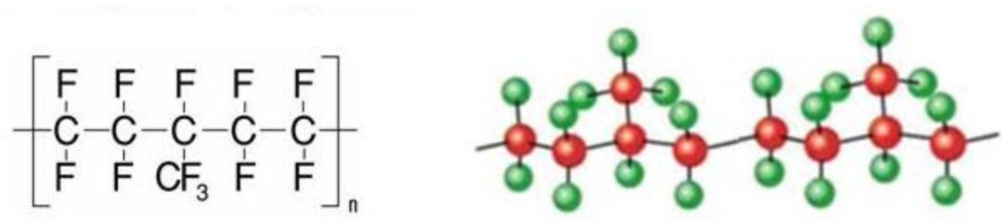

Figure 5: Molecular structure of fluorinated ethylene propylene, commonly known as Teflon® FEP.[10]

PFE is a good candidate for two reasons. The low surface energy could potentially prevent calcium carbonate from adhering by limiting its ability to nucleate. Or, it may not limit deposition significantly but may make mechanical removal easier. Two slightly different FEP coatings were chosen as representative samples (Figure 6).

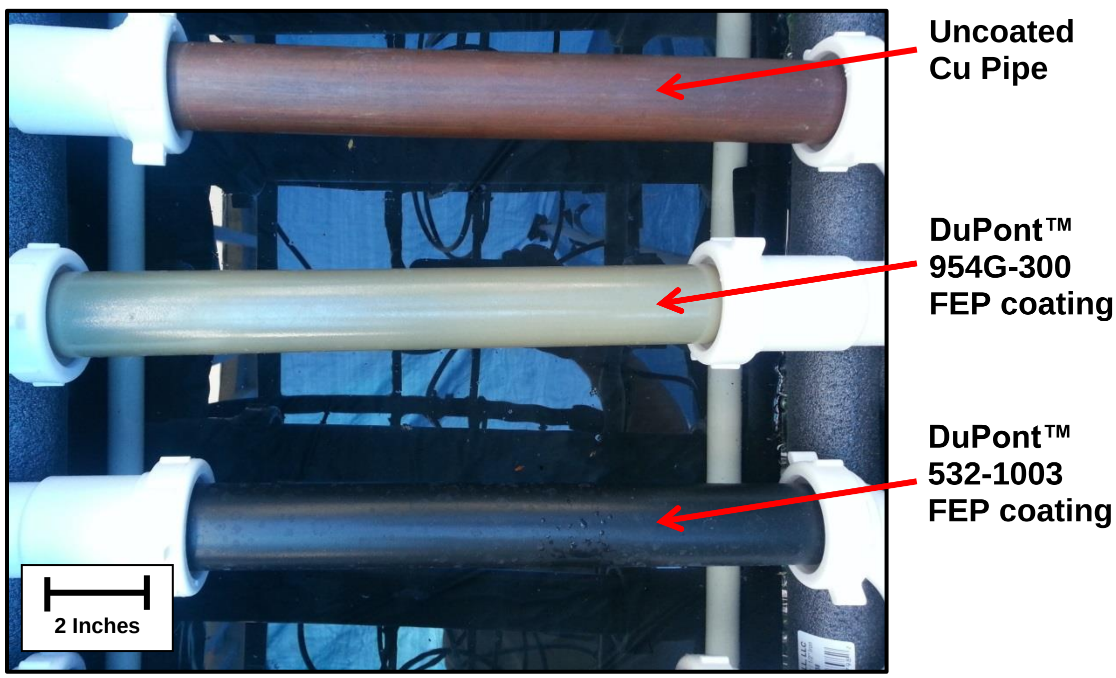

Figure 6: Three standard 1.25" diameter by 1' copper pipes. The bottom two samples have been coated with fluorinated ethylene propylene.

2.1.1.1 DuPont™ 954G-300 One Coat Industrial Nonstick Coating

The olive green coating (Figure 7) is a solvent-based self-priming, one-coat fluoropolymer blend with other resins. It was applied as an exterior coating to five independent foot-long lengths of 1.25-inch diameter copper pipe. A conventional industrial electrostatic spray gun was used to coat the cleaned surface. One coat was applied with an average thickness of 1.2 mils. For one coat, the bake time for proper curing was 10 minutes at 500°F.

2.1.1.2 DuPont™ 532-1003 One Coat/Primer Industrial Nonstick Coating

The black coating (Figure 7) is a powder-based self-priming, one-coat fluoropolymer blend with other resins and was applied as an exterior coating to five independent foot-long lengths of 1.25-inch diameter copper pipe. A conventional industrial electrostatic powder spray gun was used at a voltage between 60-80 KV. The surface was cleaned to improve adhesion. One coat was applied with an average thickness of 0.8-1.5 mils. For one coat, the bake time for proper curing was 10 minutes at 400°F.

2.2 Functional Requirements

Drill Cool Systems, Inc. imposed two functional requirements: the copper pipe bundle must maintain a temperature of 200°F and the source water must be extremely hard (1000 ppm calcium). Other considerations included that the scaling deposit rate would increase if the water was evaporating off of the pipe surface, as opposed to being constantly submerged. Additionally, the pipes would have to be easily installed and removed for setup and analysis. The system, if designed properly, could also be used for future testing of alternate coatings. It was decided that the best way to replicate the operating conditions was to build a simulated evaporative heat exchanger with replaceable heat exchanger pipes.

2.3 Realistic Constraints

2.3.1 Economic Constraint

Budget constraints for this project were considered in two separate areas. Regardless of the results observed concerning the viability of fluoropolymer coatings as a solution, any changes made to the DCS cooling units would have to be profitable. In other words, if the current method of removal is less expensive than upgrading the system then the upgrade is not practical. No specific monetary constraints were established other than that the final solution must be “cost effective.” The second budgetary constraint considered was with regard to the experimental setup. While DCS did provide funding, it was limited. The simulated heat exchanger had to be built using fairly common parts that could be purchased for a reasonable amount of money. Additionally, instruments and parts already owned by the university and available for use were considered as a means to stay within the allocated budget.

2.3.2 Manufacturability Constraint

While polytetrafluoroethylene (PTFE) was the desired coating, it was not a viable option due to a copper oxide layer that forms during the high temperature PTFE cure (650°F). This oxide layer forms an undesirable layer in between the copper and the PTFE. The oxide layer effectively blocks proper adhesion between the two materials and the integrity of the coating cannot be guaranteed. New coating considerations remained in the fluoropolymer family but now the field of possibilities was limited by cure temperatures. PTFE cures at 650°F, anything close to or above that could not be considered.

2.4 Experimental Design

There were four main components to the simulated heat exchanger: the water reservoir, the water delivery system, the heat exchanger pipes, and the means by which the system is heated to 200°F.

2.4.1 Water Reservoir

Because the water source was required to maintain a hardness concentration of 1000 ppm calcium, an open source water delivery system was not an option. Maintaining such a high calcium concentration and consuming that supply would require too much calcium. A system with a recycled water supply was necessary. As such, a standing water reservoir was employed containing a volume between 120-140 liters of water (Figure 7). 1000 ppm calcium concentration was achieved by dissolving calcium chloride ($CaCl_2$) into the reservoir at 1 gram $CaCl_2$ per 1 liter of water. The reservoir was constructed using black polyethylene sheeting.

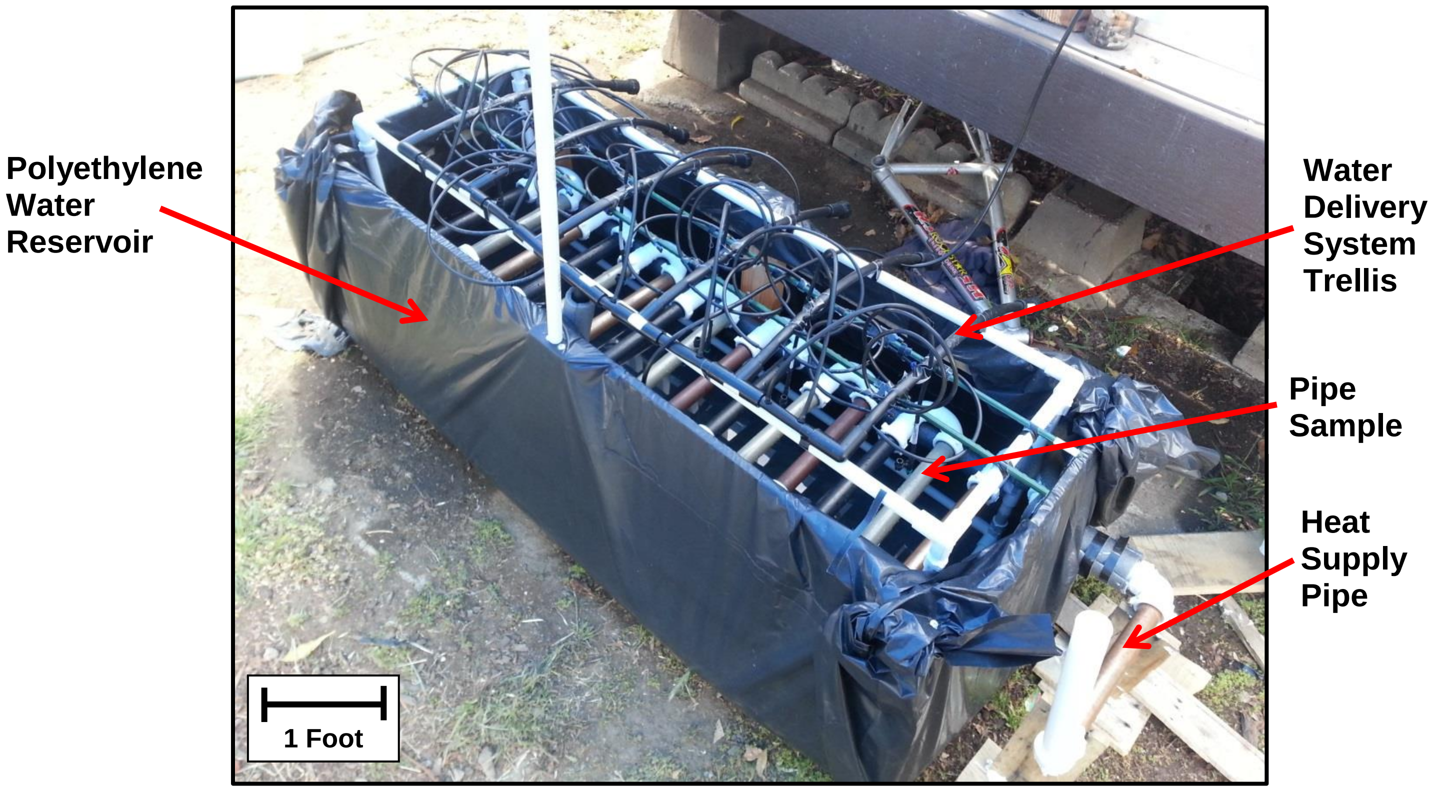

Figure 7: The simulated evaporative heat exchanger. Note the black polyethylene plastic water reservoir.

2.4.2 Water Delivery System

The water delivery system would ideally replicate the spray conditions observed in a DCS evaporative cooler. The main considerations made were to ensure complete water coverage of the pipe samples and that the water was sprayed such that the samples were not effectively submerged. A DIG Corp. drip irrigation system was purchased from the hardware store along with DIG Corp. 90 Degree Spray Jets. The Poly Drip Tubing was cut and assembled in line with a TotalPond 530 gallon per hour pond pump (Figure 8).

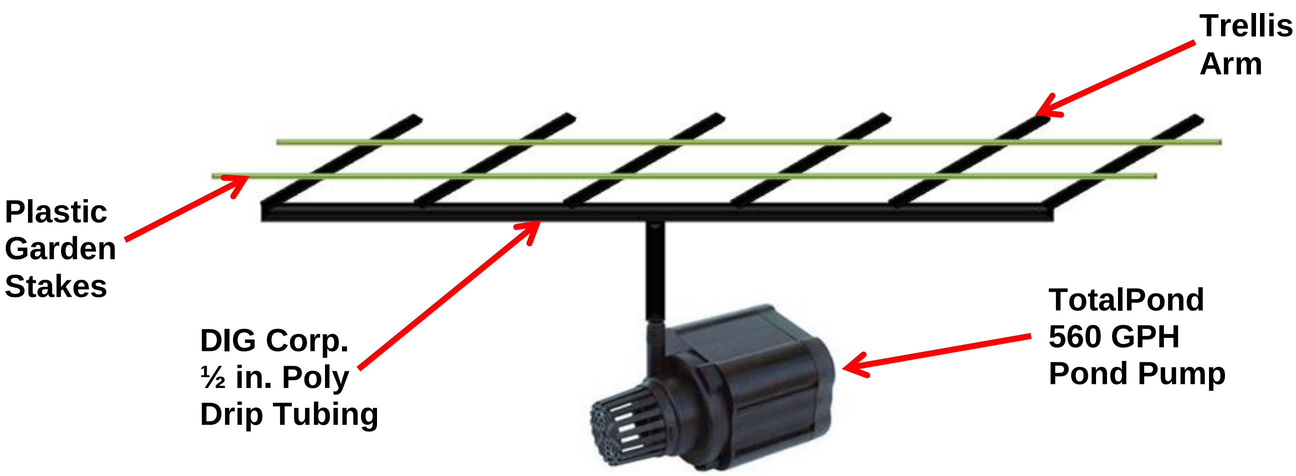

Figure 8: A representation of the irrigation hose trellis in line with the pond pump. The 90 degree spray jets attach to the ½ in. Poly Drip Tubing using ¼ in. DIG Corp. Dripline and are supported by the plastic garden stakes.

Two 90 Degree Spray Jets were placed directly over each pipe sample for complete and even coverage. Additionally, a DIG Corp. Mini Sprinkler was hung from each trellis arm to ensure spray coverage. The sprayers and tubing were housed directly above and surrounded by the water reservoir so that as water is sprayed over the pipe samples, it drops back into the reservoir to be recycled. The pond pump has an adjustable flow rate, so flow rates may be varied.

2.4.3 Heat Exchanger Pipes

The pipes were required to operate at 200°F to simulate hot mud inflow. The pipes were connected so they could be filled with heated water that would maintain the system at 200°F. Polypropylene kitchen drain traps were used because of their relatively high maximum operating temperatures. They were set up in conjunction with the pipes, using plastic seals to avoid leakage, alternating one sample after the other (Figure 9) until all fifteen pipe samples were connected.

Figure 9: The pipe samples were connected to form a watertight seal using polypropylene drain traps and their associated seals. All fifteen samples were connected alternating and were open to the atmosphere on both ends.

2.4.4 Temperature Control

An Omega CSI32K miniature benchtop controller and Omega FWH321-020 high temperature heat tape were integrated into the system because of their availability from the university. A means of heating was necessary and these two components could provide that. A separate copper pipe, outside of the water reservoir system (Figure 10), was attached to the fifteen samples in a similar fashion to Figure 9.

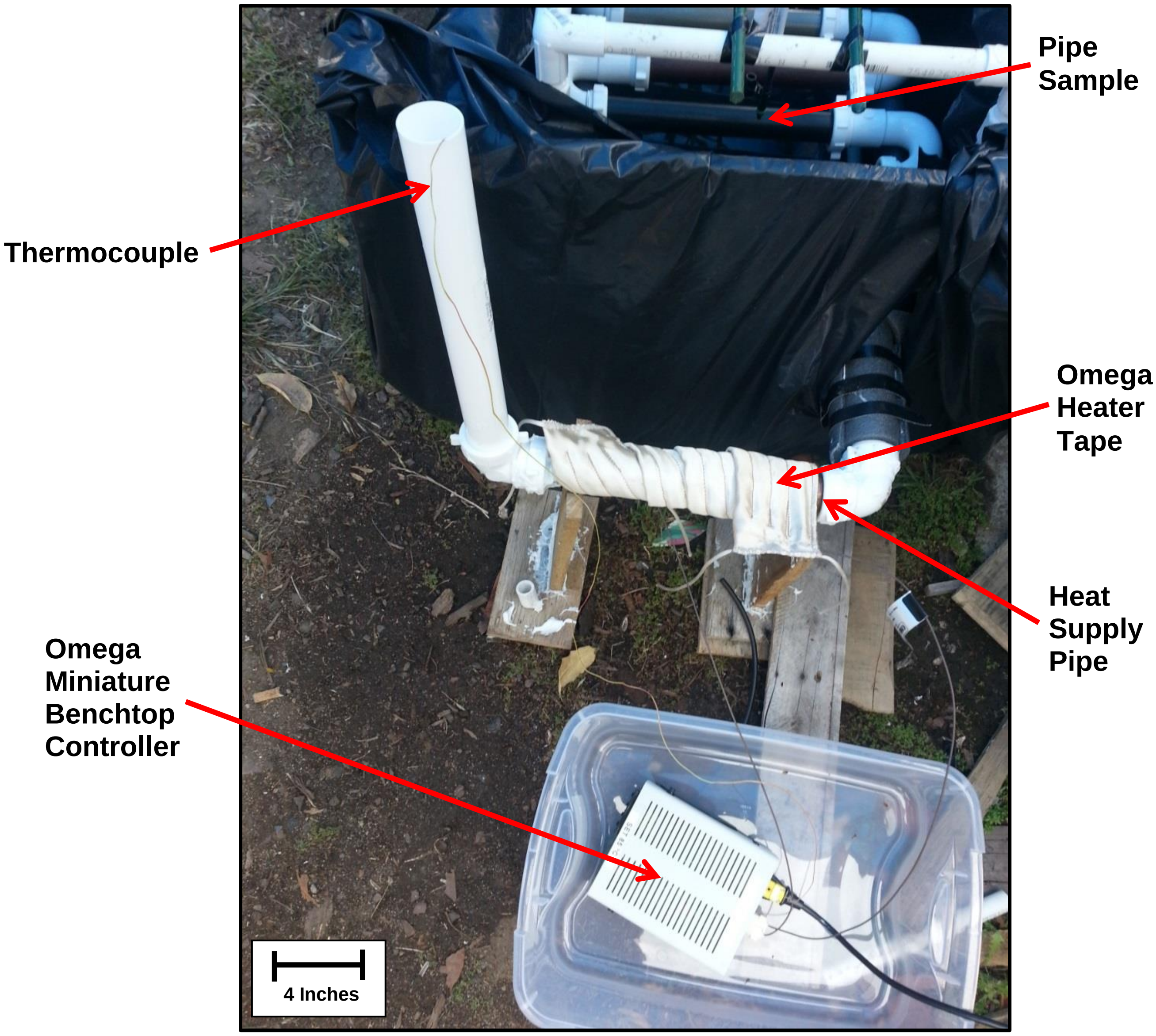

Figure 10: The heater tape is wrapped around the heat supply pipe, which is filled with water and connected to the fifteen pipe samples. A thermocouple attached to the Omega miniature benchtop controller and placed in the water supply regulates the temperature by switching the heater tape on and off.

The heat supply pipe was setup to transfer heat by conduction. This happens in a two-phase process. The heater tape conducts heat through the copper pipe to the water and then the heat gets dispersed through the water, also by conduction. Without deliberately mixing the water in the sample pipes, this method of heating relies solely on heat transfer through conduction.

2.5 Experimental Setup

The water reservoir was filled and a sufficient amount of $CaCl_2$ was added (1g/L of water) to achieve a concentration of 1000 ppm calcium. The sample pipe assembly was filled with water and the controller was set to heat the system up to 200°F. The temperature of the system was monitored until the system reached equilibrium at 200°F. At this point, the pond pump would be turned on and the system would run (Figure 11) until a sufficient amount of scale had built up.

Figure 11: The simulated evaporative heat exchanger in operation at ambient temperature (no heat input from Omega heater tape).

This determination was to be done qualitatively as there was no way to effectively predict the amount of scale buildup in a certain time frame. At the point where sufficient buildup was achieved, the pipes were to be removed from the assembly and ASTM D 3483 – 05 was to be used to determine weight of scale buildup per unit area.[10]

3 Results

No calcium carbonate buildup was seen as the system did not work properly. The system could only maintain a temperature of 200°F in the direct region surrounding the heater tape while the system was not in full operation (sprinkler system not running). After four hours of attempted heating, the pipe directly adjacent to the heat supply pipe reached and maintained a temperature of approximately 170°F, while the pipe on the opposite end of system remained at ambient temperature. This state of the system was monitored for another 2 hours; no appreciable changes were observed.

4 Discussion

Three of the four design components (the water reservoir, the water delivery system, and the heat exchanger pipes) performed well. The water reservoir provided an easy solution to the problem of maintaining a constant water supply with a high mineral concentration. The polyethylene sheeting provided a sufficiently strong system into which water and $CaCl_2$ could easily be added. The reservoir also worked well in that it did not leak water or allow water being sprayed to leave the system, unless evaporated. The DIG Corp. irrigation system and the pond pump performed well and maintained complete water coverage of the pipe samples without effectively submerging them. The pipe samples were easily installed and removed using the polypropylene drain trap fittings. The entire system was completely water tight, and it had no pressure buildup problems because both ends of the pipe assembly were open to the atmosphere. The problems arose in the fourth design component, the temperature control.

The heater tape provided insufficient heat energy to maintain the system at 200°F. As water at ambient temperature sprayed over the heat exchanger surfaces, any built up heat in the system was immediately cooled. This was a good indication that the heat exchanger would work properly as a cooling unit but was not helpful in analyzing scale deposition rates.

Modifications were made to the system in order to attempt to solve the problem. Initially, in an attempt to lessen the load put on the heater tape, boiling water was added to the pipe assembly. While this method helped to increase the speed at which the maximum heat was achieved, it still was not sufficient as the cooling ability of the unit was too great for the heater tape. Again, the water in the region of the heater tape, at times, would maintain a near boiling temperature. This suggested that the water required more circulation to benefit from the full capacity of the heater tape.

To test this theory, a basic drill pump was added to the pipe assembly and a loop was created using rubber heater hose. The drill pump provided a means to move the water through the assembly and the loop provided a path. The thought was that the water was not conducting enough heat and needed to flow (convection). An improvement in the system temperature was observed in that a greater number of its parts got warmer; however, the heater tape still provided nowhere near enough energy.

Additionally, the pipe assembly was reduced from fifteen samples to three samples. This greatly reduced the amount of water that needed to be heated and reduced the cooling capacity of the exchanger. Even with this significant scale back, the system was unable to maintain a sufficient temperature to evaporate the water being sprayed.

5 Conclusions

1. The simulated evaporative heat exchanger works in its function to provide an interchangeable pipe testing system capable of delivering a constant mineralized water spray.
2. The simulated evaporative heat exchanger works in its function to cool that which is flowing through the pipe assembly.
3. The Omega FWH321-020 high temperature heater tape does not provide sufficient energy to maintain the entire system at 200°F.

6 References

1. "The Drill Cool Systems Advantage." *Drillcool.com*. Drill Cool Systems, Inc., 2001. Web. 01 Feb. 2013.
2. Champness, Al T., Anthony J. Worthen, and John T. Finger. *Preliminary Design of Insulated Drill Pipe for High Temperature, High Pressure Drilling*. Rep. no. Project No. NT42951. Bakersfield: Drill Cool Systems, 2007. *TOPICAL REPORT*. National Energy Technology Laboratory. Web. 1 Feb. 2013.
3. "Evaporative Cooler." *Wikipedia*. Wikimedia Foundation, 31 May 2013. Web. 07 June 2013.
4. "Copper." *Wikipedia*. Wikimedia Foundation, 06 June 2013. Web. 07 June 2013.
5. Crabtree, Mike, David Eslinger, Phil Fletcher, Matt Miller, Ashley Johnson, and George King. "Fighting Scale - Removal and Prevention." *Oilfield Review* (1999): 30-45. Schlumberger. Web. 1 Feb. 2013.
6. "Formation of Hard Water Scale." *Precipitation Fouling Due to Hard Water in Household Appliances and Its Effects on Homeowners*. Tangient, n.d. Web. 07 June 2013.
7. Bansal, B., X. Chen, and H. Mullersteinhagen. "Analysis of ‘classical’ Deposition Rate Law for Crystallisation Fouling." *Chemical Engineering and Processing: Process Intensification* 47.8 (2008): 1201-210. Print.
8. "Surface Energy Data for FEP: Fluorinated Ethylene Propylene, CAS # 25067-11-2."*Accudynetest.com*. Diversified Enterprises, 2009. Web. 7 June 2013.
9. "Carbon-fluorine bond." *Wikipedia*. Wikimedia Foundation, 20 May 2013. Web. 07 June 2013.
10. ASTM Standard D 3483 – 05, 2009, “Standard Test Methods For Accumulated Deposition In a Steam Generator Tube,” ASTM International, West Conshohocken, PA, 2009, www.astm.org.